

Kinetic exchange vs. room temperature ferromagnetism in diluted magnetic semiconductors

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Abstract

Guided by the internal-reference rule and the known band offsets in III-V and II-VI diluted magnetic semiconductors, we discuss the feasibility of obtaining p-type conductivity, required for the carrier-induced ferromagnetism, as well as the cases for which the doping by shallow impurities may lead to the ferromagnetism driven by the double exchange. We consider the dependence of kinetic exchange on the p-d hybridization, on the electronic configurations of the magnetic ions, and on the energies of the charge transfer between the valence band of host materials and the magnetic ions. In the case of Mn-based II-VI compounds, the doping by acceptors is necessary for the hole-induced ferromagnetism. The latter is, however, possible without any doping for some of Mn-, Fe- or Co-based III-V magnetic semiconductors. In nitrides with Fe or Co carrier-induced ferromagnetism with $T_C > 300$ K is expected in the presence of acceptor doping.

The discovery of the ferromagnetic order in Mn-based III-V [1, 2, 3, 4] and II-VI diluted magnetic semiconductors (DMS) [5, 6] started intensive studies of these materials and their layered structures [7, 8]. The recently demonstrated phenomena, such as spin-injection from (Ga,Mn)As contacts [9], tuning of magnetic properties by an electric field [10], and large tunneling magnetoresistance [11], brought closer the idea of new semiconductor spin devices combining complementary features of semiconductor and magnetic systems. For this purpose it is, however, of great importance to increase the Curie temperatures of ferromagnetic DMS. Much technological effort has been recently put in the search for different DMS exhibiting ferromagnetism at room temperature. The hope for finding such materials was awakened when the Curie temperatures above room temperature was predicted for materials containing light anions [12]. To explain the origin of the ferromagnetism in tetrahedrally coordinated DMS as well as the values of the Curie temperatures the mean-field Zener model was employed [12]. In this model, the ordering of spins results from the p-d kinetic exchange interaction between the magnetic ions and the delocalized or weakly localized holes. Accordingly, the large value of the exchange energy $N_0\beta$ is one of the crucial conditions for high-temperature ferromagnetism, along with the large (of the order of few 10^{20} cm⁻³) hole and Mn concentrations. We note that in n-type DMS, only very low Curie temperatures can be expected because of small s-d exchange energy and low density of states in the conduction band [13]. Indeed, no ferromagnetism was detected above 1 K in (Zn,Mn)O:Al [14].

The values of $N_0\beta$ are well known for many of the II-VI DMS which have been extensively studied in the last two decades [15, 16]. In contrast, the available information on this constant in III-V DMS concerns primarily GaAs with Mn²⁺ ions – for this material several values, ranging from -0.9 eV [17] and -1 eV [18] to -4.5 eV [19] have been suggested. At present, the most reliable seems to be the value $N_0\beta = -1.2$ eV inferred from the photoemission data [20]. The latter value (scaled by the inverse volume of the elementary cell) was used for predicting the Curie temperatures for various III-V DMS with Mn²⁺ (i.e., d⁵-configuration) ions [12].

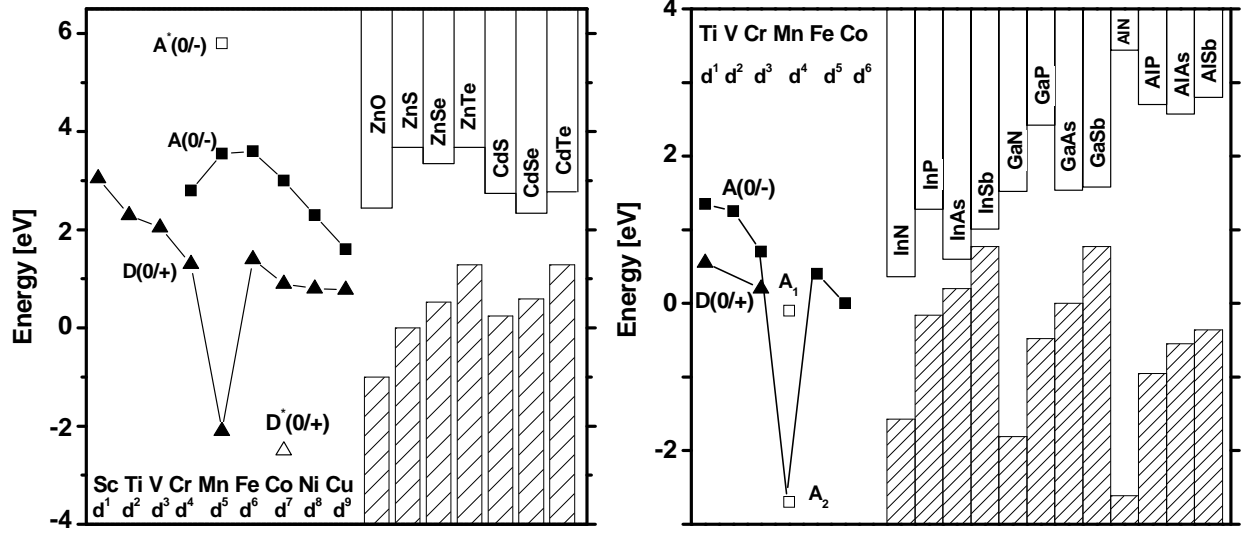


FIG. 1: Approximate positions of transition metals levels relative to the conduction and valence band edges of II-VI (left panel) (after [16, 22, 23, 24, 25, 26, 27, 28]) and III-V (right panel) (after [22, 24, 29]) compounds. By triangles the d^N/d^{N-1} donor and by squares the d^N/d^{N+1} acceptor states are denoted; in (left) the solid symbols represent the ground states, whereas the open symbols the excited final states with lower spin values. In (right) the states labeled A_1 and A_2 correspond to the d^4/d^5 acceptors as given by spin-resonance studies in GaP:Mn [30] and by photoemission in (Ga,Mn)As [20], respectively.

In this paper, we discuss the position of electronic states introduced by transition-metal impurities in II-VI and III-V compounds from the view point of ferromagnetism mediated either by band carriers or double exchange. We show also a strong dependence of the p-d exchange energy on the number and configuration of the electrons residing on the d shell of various magnetic ions.

According to the internal reference rule [21, 22], the positions of states derived from d shell of magnetic ions do not vary across the entire family of the II-VI or III-V compounds if the valence band offsets between different compounds are taken into account. In Fig. 1 (left panel) we present the collected data for the II-VI DMS containing various transition metal ions. We have denoted by $D(0/+)$ and $A(0/-)$ the donor and acceptor levels (i.e., the lower and upper Hubbard bands), which correspond to the transformation of the doubly ionized magnetic ions M^{2+} into M^{3+} and into M^{1+} ions, in their ground states, respectively. By $D^*(0/+)$ and $A^*(0/-)$ we denote the excited donor and acceptor levels, with lower spin than the corresponding ground states. Energies of these levels enter the formulae that determine the exchange energy (see Eqs. 1 and 2).

Some information about the possibility of the hole induced ferromagnetism in II-VI DMS can be directly obtained from Fig. 1. First of all, we observe that the doping with shallow acceptors is necessary to obtain the p-type materials as the acceptor levels of all the transition metal ions lay well above the top of the valence band of every II-VI compound. Moreover, one can see that for all transition metals with $N \neq 5$ (perhaps apart from Co in the tellurides) also the donor level lays above the valence band and, thus, the appearance of the band holes (even with an additional acceptor doping) is excluded. From this point of view, the Mn^{2+} ($N = 5$) ion is quite unique, since its donor level is situated well below the top of the valence band of all the II-VIs, giving the chance for p-type DMS. Indeed, in (Cd,Mn)Te and (Zn,Mn)Te doped with N or P the hole-induced ferromagnetism was observed between 1 and 3 K [5, 6, 14]. In view of the above discussion, we note that the recently reported room-temperature ferromagnetic behavior of

n-type (Zn,Co)O [31] and (Zn,V)O [32] layers cannot be attributed to the carrier induced mechanism described by the Zener or RKKY model. The data may suggest that double exchange involving hopping of electrons over acceptor levels (upper Hubbard band) is involved. We note, that for V ions in II-VIs also the superexchange was predicted to be ferromagnetic, [33].

It should be, however, noted at this point that the internal reference rule may serve only for the illustration of chemical trends and not for extracting the precise values of the ionization energies. Moreover, in DMSs other states related to the magnetic impurities may also appear, e.g.[34]. Strong p-d hybridization can lead to binding of a hole in a Zhang-Rice polaron, which then gives rise to an additional state in the band gap [35, 36]. Furthermore, if the d^N/d^{N-1} donor level resides above the bottom of the conduction band, the ground state corresponds to a hydrogenic-like donor level $d^{N-1}+e$ located below the band edge, as observed in CdSe:Sc [37]. Similarly, if the acceptor state is located under the top of the valence band, the ground state corresponds to a hydrogenic-like acceptor $d^{N+1}+h$, not to the d^N state. Obviously, energies of hydrogenic-like states follow the band edges, and by no means are described by the internal reference rule. This appears to be the case of the Mn related levels in III-V compounds [36]. These effects cause some ambiguity concerning the nature of states observed experimentally in magnetically doped semiconductors.

To examine chemical trends in III-V DMS we present in Fig. 1 (right panel) the literature data concerning valence band offsets and energy levels of transition metal impurities for the III-V semiconductors. Here D(0/+) and A(0/-) denote again the donor and acceptor states, which, in contrast to the situation in II-VI DMS, correspond to the transformation of the triply ionized magnetic ions M^{3+} into M^{4+} and into M^{2+} ions, respectively. The energies of all but Mn transition metal impurity levels (solid symbols in Fig. 1) were taken from Ref. [22]. The position of Mn acceptor A(0/-) level with respect to the valence band edges of the III-V-s is not conclusively established. According to optical and EPR experiments in GaP:Mn, the Mn d^4/d^5 level is located at 0.4 eV above the valence band edge (A_1 in Fig. 1) [30]. On the other hand, the analysis of photoemission in (Ga,Mn)As [20] suggests this level to reside deep (~ 2.7 eV) below the valence band edge (the A_2 position). The latter position of the Mn d^4/d^5 level is consistent also with the occupation number of the Mn d-states close to 5, inferred from the x-ray magnetic circular dichroism [38], and with the results of the LSDA+U computations [39]. In the following we show that these two (A_1 and A_2) positions, when used as the input values for the internal reference rule, lead to quite different conclusions about the ferromagnetism in Mn based III-V DMS.

From Fig. 1 one can see that the chances of obtaining the p-type in III-V are better than in II-VI DMS. With the position A_2 of the Mn d^4/d^5 acceptor level the large concentration of holes in the valence band can be obtained in all presented III-V compounds without any additional doping. Thus, the conditions required for the ferromagnetism in the Zener model are fulfilled in all these compounds [36], except perhaps AlN. In GaSb and InSb the same can be expected even if the Mn d^4/d^5 level position is A_1 and also for Co-based DMS. The antimonides are, however, less promising for high temperature ferromagnetism, because of their relatively large lattice constants and, consequently, weak p-d hybridization. For Fe in GaSb and InSb and for Co and Mn (A_1) in GaAs and InAs the internal reference rule implies the acceptor level slightly below the valence band edge, i.e., the p-type with relatively low concentrations of delocalized holes can be expected. In such case the Fermi level, after reaching the acceptor level position, would remain pinned to it. The coexistence of the M^{2+} and M^{3+} ions would open an additional channel of the exchange interaction, namely, the ferromagnetic double exchange, as proposed [40] for uncompensated (In,Mn)As. In materials in which the acceptor A(0/-) level is situated within the band gap, the p-type can be obtained only by shallow acceptor doping. This requires, however, the donor level to reside below the valence band edge. According to Fig. 1, in the case of Ti and Cr ions, the

p-type samples seem to be excluded.

Within the second order perturbation theory the kinetic exchange can be described in terms of hybridization-induced virtual transitions of electrons between the band and the ionic d-shell. In the case of II-VI diluted magnetic compounds it was shown that the kinetic exchange mechanism depends crucially on the electronic configuration of the magnetic ions [41] and the charge transfer energies for the transitions from the band onto the magnetic ion and vice-versa [33]. For the p-band in the vicinity of the Γ point, the transitions only to/from the ionic t_{2g} orbitals are allowed. For tetrahedrally coordinated DMS with various magnetic ions, the contribution to the kinetic exchange from the transitions involving singly occupied orbitals is proportional to the exchange constant [15]:

$$N_0\beta_N = -\frac{V_{pd}^2}{S} \left[\frac{1}{E_{N-1}^{S-1/2} + \epsilon_p - E_N^S} + \frac{1}{E_{N+1}^{S-1/2} - \epsilon_p - E_N^S} \right] \quad (1)$$

whereas the contribution involving empty t_{2g} orbitals is proportional to:

$$N_0\gamma_N = \frac{V_{pd}^2}{(S+1/2)} \left[\frac{1}{E_{N+1}^{S+1/2} - \epsilon_p - E_N^S} + \frac{1}{E_{N+1}^{S-1/2} - \epsilon_p - E_N^S} \right] \quad (2)$$

where V_{pd} can be related to the Harrison inter-atomic matrix elements:

$V_{pd} = \frac{4}{3}(V_{pd\sigma} - 2V_{pd\pi}/\sqrt{3})$; E_N^S is the energy of the ion with N d-electrons and the total spin S ; ϵ_p is the energy of the electron at the top of the p-band. It has been also shown that for ions with all t_{2g} orbitals occupied by the same number of electrons, the kinetic exchange leads to the Kondo-like Hamiltonian, with the exchange constant $N_0\beta$ for ions with d^5 , d^6 or d^7 electronic configurations and with $N_0\gamma$ for the d^1 and d^2 ions [41]. For other electronic configurations the kinetic exchange Hamiltonian is more complex and depends on the ionic orbital degrees of freedom – still, for the d^3 and d^4 ions the Kondo-like form of the Hamiltonian can be restored by the static Jahn-Teller effect (provided the cubic symmetry is in average conserved) with the exchange constant being an appropriate combination of $N_0\beta$ and $N_0\gamma$.

The values and even the signs of all exchange constants depend on the charge transfer energies in the denominators in Eqs. (1) and (2), which are related to the distances between the donor or acceptor levels and the edge of the valence band.

As predicted previously [12], among the II-VI DMS the best candidate for the hole-induced, high temperature ferromagnetic system seems to be (Zn,Mn)O. In this compound one expects the value of the exchange energy to be considerably greater than in the other II-VI DMS. This is due to the small elementary cell of ZnO, which results in the large hybridization constant V_{pd} . The phenomenological scaling used in [12] leads to the value of $N_0\beta$ in ZnO:Mn equal to -2.48 eV. A comparable value, $N_0\beta = -2.1$ eV, was recently obtained in Ref. [42] with the parameters entering to Eq. (1) determined by the best fit to the photoemission spectra. The value obtained with the charge transfer energies given by the internal reference rule in the Fig. 1 and the Harrison hybridization parameters is even larger, i.e., -3.2 eV.

In a given host material the values of the $N_0\beta$ constant are known to be considerably larger for Co than for Mn ions. This is primarily due to the smaller value of spin S in the denominator of Eq. (1), since the charge transfer energies are similar in both cases (note that for Co^{2+} ($N=7$) the charge transfer energy not from the $D(0/+)$ but from $D^*(0/+)$ enters Eq. (1)). Unfortunately, this enhancement of the exchange constant is compensated by the decrease of magnetic susceptibility (proportional to S^2). Thus, one should expect similar Curie temperatures for the p-type tellurides with Mn and Co ions – relatively low, due to their large lattice constants.

In III-V DMS the strongest hybridization favoring the high temperature ferromagnetism is expected in phosphides and nitrides. In these compounds the acceptor levels of Fe and Co are

situated above the valence band. Thus, in p-type samples the charge state of these ions would remain the same as of the host cations and their electronic configurations are d^5 and d^6 , respectively. The estimated in [43] values of $N_0\beta$ [-2.8 eV in (Ga,Fe)N and -3.1 eV in (Ga,Co)N] suggest that in these compounds, the ferromagnetism with $T_C > 300$ K could be expected, provided that a high concentration of holes can be introduced. Preliminary data on (Ga,Fe)N, with the low Fe content (of the order 10^{19} cm $^{-3}$) have already revealed ferromagnetic properties below 100 K [44].

To evaluate the prospects of obtaining ferromagnetic Mn-based nitrides and phosphides with high Curie temperature the discrimination between the positions A_1 and A_2 of the d^4/d^5 acceptor level is of primary importance. This is because, with the gap position A_1 an additional doping would be necessary to obtain the p-type material, and the electronic configuration of the ions would be d^4 , which is *not* favorable for high T_C . In this configuration, due to a partial cancellation of two terms, the antiferromagnetic $N_0\beta$ and the ferromagnetic $N_0\gamma$, the kinetic exchange would be considerably reduced [43]. The first samples of (Ga,Mn)N reported in the literature [45] seemed to be of n-type with ionized (d^5) Mn acceptors. The position of the acceptor level at about 1 eV above the valence band edge, deduced from optical measurements [46], suggests the above described scenario in the hypothetical p-type samples. This position does not fulfill, however, the internal reference rule with either A_1 or A_2 positions. It may be rather ascribed to the binding energy of holes in Zhang-Rice polaron states bound to d^5 Mn acceptors [36]. This interpretation selects the A_2 position of the Mn d^4/d^5 acceptor level, deep in the GaN valence band. With this position and, therefore, the d^5 configuration of Mn ions in the p-type material, the Curie temperatures well exceeding 300 K were predicted within the Zener model [12, 36], in consistence with the recently reported indications of ferromagnetic transitions in (Ga,Mn)N [47, 48, 49].

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